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Solid state organisation of C_{60} by inclusion crystallisation with triptycenes†

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Triptycene and azatriptycene act as concave receptor molecules for C_{60}, resulting in the solid state organisation of C_{60} in a layered and a hexagonal pattern, respectively.

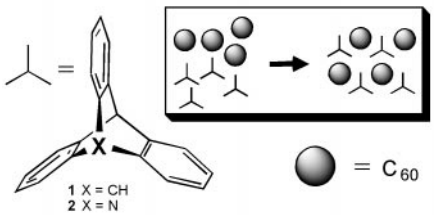
Fullerenes are of considerable interest in the design of novel materials as the strong electron acceptor properties associated with C_{60} result in intriguing optical and semiconductor phenomena.[1] The controlled organisation of C_{60} in stacks or arrays by crystal engineering and host–guest chemistry plays a decisive role in these efforts.[2,3] The solid state structures of a number of inclusion complexes and supramolecular arrays of fullerenes have been reported in recent years.[4,5] An emerging structural feature in controlling the delicate host–guest interactions is geometrical complementarity of the globular C_{60} guest and dish or saddle shaped host molecules.[2,5,6] Here we report a simple method to achieve the solid state organisation of C_{60} by inclusion crystallisation with triptycene. In addition a change in organisation, by modification at a single position in the host molecule, as shown by X-ray analysis of the inclusion complexes was observed.

We envisioned that the combination of star-shaped triptycenes, with three concave faces, and C_{60} with its convex surface might lead to self-assembly as shown in Scheme 1.

The inclusion complex of C_{60} and triptycene **1** was obtained as dark red crystals from a hot *o*-xylene solution, by slow evaporation of part of the solvent over several days. NMR, IR and chromatographic analysis established an inclusion complex of C_{60}, triptycene and *o*-xylene. X-Ray structure analysis confirmed the composition in a 1:2:2 ratio respectively. The molecular structure is shown in Fig. 1(*a*).‡

The inclusion complex has centric [monoclinic space group *P*2(1)/*c*] symmetry in the solid state. The fullerene molecules pack in an approximate hexagonal close packed sphere pattern parallel to the *bc*-plane with translation vectors 9.9958(11) (= *b*-axis) and 10.1468(11) Å [= $\frac{1}{2}$(*b*+*c*)].

The packing arrangement is shown in Fig. 2. Adjacent triptycenes stack in an antiparallel fashion generating two concave surfaces in opposite directions. Each C_{60} is capped by two molecules of **1** [Fig. 1(*a*)] and the closest distance between the two flanking arene groups of each triptycene (dihedral angle 120°) and C_{60} of approximately 3.27 Å§ is significantly shorter than those reported for calixarene and related complexes (3.51–3.62 Å).[6]



Scheme 1

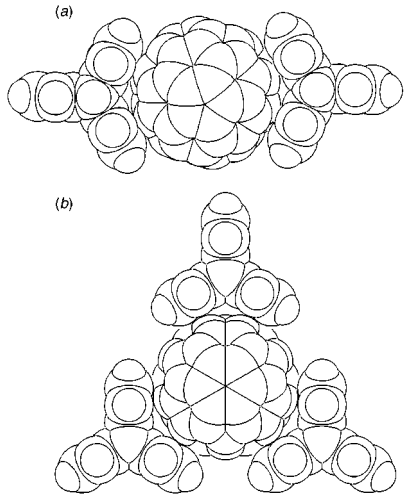


Fig. 1 (*a*) Moleculer structure of C_{60} and triptycene (**1**) (*o*-xylene omitted for clarity). (*b*) Molecular structure of C_{60} and azatriptycene (**2**).

The C_{60} molecules are arranged in sheets composed of one-dimensional strands in the *bc*-plane to achieve a close packing of spheres in the sheets. The shortest $C_{60}\cdots C_{60}$ separation of 3.08 Å¶ is close to that found in other linear strands.[2] Each sheet is separated by a double layer of antiparallel oriented triptycenes and *o*-xylenes with the latter filling voids between the

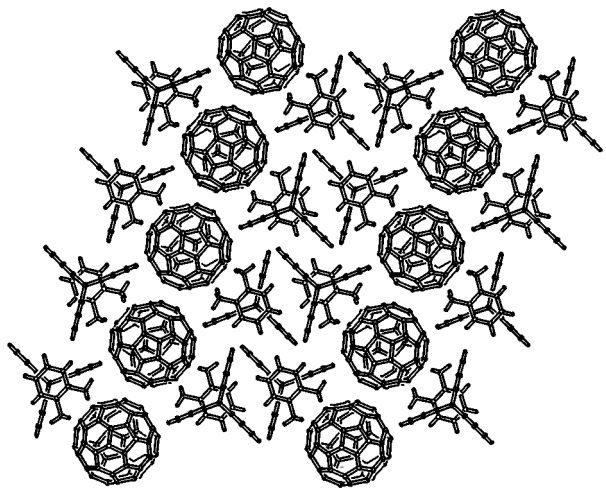


Fig. 2 Packing arrangement for the complex of C_{60}, *o*-xylene and triptycene.

† Colour versions of Figs. 1–3 are available from the RSC web site, see http://www.rsc.org/suppdata/cc/1999/1709/

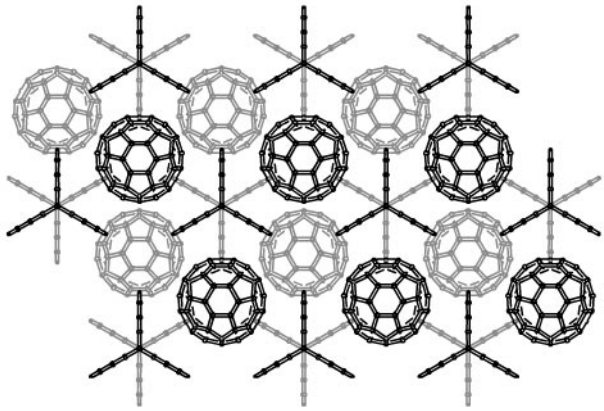


Fig. 3 Packing arrangement for the complex of C_{60} and azatriptycene.

triptycenes in this double layer. The nearest neighbour C_{60} molecules in two adjacent layers are 18.58 Å apart.

As the rigid concave triptycene has a favourable receptor shape to allow the formation of supramolecular arrays of C_{60} its molecular architecture might be suitable to change the assembly formation by modifying in the host–guest interactions. Introduction of a nitrogen atom at a bridgehead position, as is the case in azatriptycene **2**,[8] was envisioned to enhance additional electrostatic interactions in the host–guest system.

Slow evaporation of part of the solvent (*o*-xylene) from a hot solution of a 1 : 1 mixture of C_{60} and azatriptycene **2** resulted in dark red crystals of the inclusion complex suitable for X-ray analysis. The molecular structure is shown in Fig. 1(*b*).‖ The hexagonal unit cell contains two C_{60} molecules and two azatriptycenes. The fullerene molecule is rotationally disordered but as each C_{60} is flanked by three molecules of **2** [Fig. 1(*b*)], whose positions are exactly determined in the crystal lattice, and as a result of the space group symmetry, the position of each fullerene is well defined.

The C_{60} molecules assemble in the hexagonal close packing pattern with each azatriptycene embracing three C_{60} molecules and each C_{60} embraced by three azatriptycene. Capping of a C_{60} molecule by three molecules of **2** results in six concave surfaces at the periphery of this ensemble which interact with a further six fullerene molecules leading to the anticipated arrangement in each layer.

The translation period in the *ab*-packing plane amounts to 13.464(1) Å (= *a*-axis). Layers are separated by 6.349(1) Å (= 1/2 *c*-axis). The closest C–C contact between both molecular species amounts to 3.40(2) Å.

The packing arrangement is shown in Fig. 3. The azatriptycenes are arranged in one-dimensional strands parallel to the *c* axis in a head-to-tail arrangement. The C_9 carbon and the central nitrogen atom of neighbouring azatriptycenes are at a distance of 3.76 Å. Each molecule of **2** in a single strand is rotated 60° with respect to its neighbour, and as a consequence each set of three concave faces in the hexagonal arrangement in a particular layer, due to a single molecule of **2**, is rotated 60° with respect to the next layer. The hexagonal packing of the C_{60} spheres is evident if one realises that the 'pillars' of the azatriptycenes generate the voids in which a C_{60} molecule in one layer is positioned exactly between six C_{60} molecules in the two adjacent layers.

The shortest intermolecular C_{60} distance (C_{60} molecules in different layers) is approximately 2.97 Å¶ which is similar to that found in the inclusion complex of C_{60} and *p*-bromocalix-[4]arene propyl ether.[2] The centre–centre distance of the azatriptycenes in one layer is 13.464(1) Å. The remarkable propensity of triptycenes to change the self-assembly of C_{60} and the fascinating structures obtained in this way are intriguing in view of the design of new host–guest systems and materials based on fullerenes.** Studies along these lines using functionalised triptycenes are in progress.

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Notes and references

‡ *Crystal data* for complex with **1**: $C_{60}\cdot 2(C_{20}H_{14})\cdot 2(C_8H_{10})$, M = 1441.54, dark red plate, space group $P2(1)/c$, a = 19.767(2), b = 9.9958(10), c = 17.661(2) Å, β = 109.882(10)°, Z = 2, V = 3281.6(6) Å^3, D_c = 1.459 g cm^{-3}, μ = 0.1 mm^{-1}, λ = 0.71073 Å, T = 150 K, θ_{max} = 25.3°. A hemisphere of reflections (11766) was scanned and averaged [R(int) = 0.15] into a unique set of 5988 reflections [2080 of which with $I > 2\sigma(I)$]. The structure was solved by direct methods (SIR97) and refined on F^2 using SHELXL97. Two sets of bond restraints were introduced in order to restrain 5-6 and 6-6 bond types. The restraints refined to 1.462(4) and 1.347(6) Å, respectively. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The displacement parameters for the C_{60} atoms display the common flat disk characteristics. Convergence was reached at R_1 = 0.0947, wR_2 = 0.261, S = 1.00, 5988 reflections, 527 parameters, 45 restraints, $-0.43 < \Delta_r < 0.64$ e Å^{-3}.

§ As a consequence of the dihedral angle of 120° in **1** and **2** the closest distance is with the C–C carbon atoms at the periphery of the (aza)-triptycenes.

¶ Based on the mean atom-to-atom diameter of C_{60} of approximately 7.07 Å (ref. 7).

‖ *Crystal data* for complex with **2**: $C_{60}\cdot C_{19}H_{13}N$, M = 975.90, dark red block, space group $P6(3)mc$ (no. 186), $a = b$ = 13.4643(11), c = 12.6983(9) Å, Z = 2, V = 1993.6(3) Å^3, D_c = 1.626 g cm^{-3}, μ = 0.1 mm^{-1}, λ = 0.71073 Å, T = 150 K, θ_{max} = 27.5°. A hemisphere of reflections (6587) was scanned and averaged (R_{int} = 0.069) into a unique set of 909 reflections [711 of which with $I > 2\sigma(I)$]. Three space groups are consistent with the observed systematic extinctions [$P6(3)mc$, P-62c and $P6(3)/mmc$]. Interpretable (partial) results (with SHELXS97 and SIR97) were obtained in both $P6(3)mc$ and its centrosymmetric counterpart $P6(3)/mmc$. In both cases it was clear that the C_{60} moiety is severely orientationally disordered. The model presented here is based on the refinement (with SHELXL97) of a restrained C_{60} 'order-model' in $P6(3)mc$. The restraint for 5-6 bonds refined to 1.480(8) Å and for 6-6 bonds to 1.290(14) Å. The unrestrained geometry of the azatriptycene is satisfactory along with the associated anisotropic displacement parameters. The anisotropic displacement parameters of the C_{60} atoms show the common flat disc shape (some non-positive definite). Hydrogen atoms were taken into account at calculated positions. Since the current refinement was stable (R_1 = 0.0861, wR_2 0.272, S = 1.05, $-0.60 < \Delta_r < 0.65$ e Å^{-3}) in the non-centrosymmetric symmetry space group description, no further attempts were made to refine a less attractive disorder model (for both moieties) required for the description in the related centrosymmetric space group. CCDC 182/1344. See http://www.rsc.org/suppdata/cc/1999/1709/ for crystallographic data in .cif format.

** The effects of C_{60}–triptycene interactions or kinetics of crystal packing on the solid state arrangement need further investigation.

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